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(54) PRODUCTION OF CARBON MATERIAL

(57) Abstract:

PROBLEM TO BE SOLVED: To obtain a carbon material having a highly controlled structure at a room temperature and a high temperature by subjecting a polyolefin derivative or an aromatic condensed cyclic hydrocarbon derivative containing a functional group eliminable as an anion to electrode electrolytic reduction.

SOLUTION: A polyolefin oligomer derivative of formula I (X1 to X4 are each F, Cl, Be, N+CR1R2R3, etc.; X5 and X6 are each as shown for X1 to X4 but X5 and X6 are not F at the same time; R1 to R3 are each C_mH_{2m+1} ($m \leq 4$); n ≤ 50) or an aromatic condensed cyclic hydrocarbon of formula II ((l) is 1, 2 or 3; C_{4l+2} is an aromatic condensed cyclic hydrocarbon group derived from benzene, naphthalene, etc.; X7 is as shown X1 to X4) is subjected to electrolytic reduction in a nonaqueous organic solvent having dissolved a

supporting electrolyte in an inert gas atmosphere. In the operation, one of magnesium, zinc and aluminum or their alloys is used as an anode in two electrode method and one of magnesium, zinc and aluminum or their alloy is as an anode in a two electrode method and as an counter electrode in a three electrode method.

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CLAIMS

[Claim(s)]

[Claim 1] The following general formula (1) It reaches (2).

[Formula 1]

that the inside of a formula, and X₁, X₂, X₃ and X₄ are the same, or two or more -- being different from each other -- F -- :X₅ which mean Cl, Br, I, H, N+CR one R₂R₃, SO₂R₁, and S+R one R₂ -- and -- X₆ is the same -- or -- being different from each other -- F -- :(however, case where both X₅ and X₆ are F is removed) R₁ which means Cl, Br, I, H, N+CR one R₂R₃, SO₂R₁, and S+R one R₂, and R₂ and R₃ It is [Formula 2] and it is the same or :n<=50 which means the alkyl group which two or more are different from each other, and is expressed with C_mH_{2m+1} (m<=4).

(:C 41+2 whose 1 is 1, 2, or 3 among a formula) :X₇ which mean the aromatic series condensed-ring hydrocarbon group guided from benzene, naphthalene, an anthracene, a naphthacene, and a pyrene F, Cl, Br, I, H, It is under [nonaqueous organic solvent / which dissolved the supporting electrolyte for at least one sort of a meltable polyolefine oligomer derivative and an aromatic series condensed-ring hydrocarbon derivative] setting. N+CR one R₂R₃, SO₂R₁, and S+R one R₂ -- meaning -- the organic solvent expressed -- The manufacture approach of the carbon material characterized by being the approach of manufacturing a carbon material by carrying out electrode reduction under an inert gas ambient atmosphere, and using one sort or these alloys of magnesium, zinc, and aluminum as a counter-electrode in three electrode methods as an anode plate in two electrode methods.

[Claim 2] A supporting electrolyte LiCl, Li₂SO₄, LiBF₄, LiClO₄ and LiPF₆, 4(C₄H₉)NF, (C₄H₉) The manufacture approach of the carbon material according to claim 1 which is at least one sort of 4NCl, 4(C₄H₉)NBr, 4(C₄H₉)NI, 4(C₄H₉)NSO₄, 4(C₄H₉)NBF₄,

4(C₄H₉)NClO₄, and (C₄H₉)₄NPF₆.

[Claim 3] The manufacture approach of the carbon material according to claim 1 or 2 which uses a supporting electrolyte and an energization assistant together.

[Claim 4] The manufacture approach of a carbon material according to claim 3 that an energization assistant is at least one sort of AlCl₃, FeCl₂, FeCl₃, CoCl₂, CuCl₂, SnCl₂, PdCl₂, VC₁₃, and ZnCl₂.

[Claim 5] The manufacture approach of the carbon material according to claim 1 which uses the solvent which contains at least 1 sorts of tetrahydrofuran, N,N-dimethylformamide, N-methyl formamide, formamide, ethylenediamine, 1, and 2-dimethoxyethane and dioxane 10% or more as a nonaqueous organic solvent.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention -- graphite, rhombohedron graphite, and a RONZUDA light -- ciao, it is related with the manufacture approach of AITO, Calvin (carbon VI *****), glassy carbon, or the carbon material that contains these at least.

[0002]

[Description of the Prior Art] There are an artificial-graphite product made by kneading with filler corks and BAINGU, baking, and graphitization, activated carbon made by carrying out activation of the ingredient which has big surface area, a car pump rack made by the pyrolysis of hydrocarbon gas, a carbon fiber further made by baking of vapor growth or an organic fiber precursor in a carbon material. However, since each manufacture approach of these carbon materials needs an elevated temperature or needs severe manufacture conditions physically, it is difficult to control the chemical structure of an ingredient to altitude. Development of a synthesis method new for manufacture of the new carbon material which controlled current and the chemical structure to altitude is furthered.

[0003] For example, since the fullerene (H. W.Kroto, et al., Nature, 318 (1985) 162) and nano CHUPU which are a new carbon material were compounded using the physical synthesis method, research which compounds the carbon material by which structure was controlled has been advanced using the physical synthesis method or the chemical synthesis method (W. Weltner, Chem.Rev., 89 (1989) 1713).

[0004] The synthesis method of the new carbon material by which structure was controlled by altitude is divided roughly into the physical approach using high energy beams, such as arc discharge and laser, and a chemical approach. The typical synthesis method reported is as follows.

[0005] one of the carbon materials -- it is -- 3-fold association and 1-fold association -- alternation -- ***** -- a line -- the synthetic approach with Calvin with structure physical in 1969 is reported (A. G.Whittakerand P.L.Kintner, Science, 165 (1969) 589). By this approach, the electrode was bound tight on both sides of the field (0001) of the square bar of PAIRORI tick graphite, and the current was held for 15 to 20 seconds in the place which reached the temperature which has 2700-3000K by the sink and resistance heating. The ambient atmosphere at this time was the argon of 10-4torr. It restricted,

when it heated 2550K or more, and the matter which shines with the silver white which has dendrite structure on some graphite rods generated. In graphite, the carbon atom carried out migration, and was formed, and this is considered that the carbon atom which carried out free evaporation agglutinated again. White will be based on scattered reflection from dendrite structure, supposing covering of the white carbon produced on the PAIRORI tick graphite front face is transparent and it is form birefringence. In this experiment, since heating is performed by ordinary pressure, high-pressure force which is imagined from a meteorite collision is not needed for composition of white carbon.

[0006] Kudryavtsey and others is compounding the carbon material including Calvin by ion sputtering and arc discharge of a graphite. The thickness of the generated film is 200-500A, and it is checking that the thing of the shape of alpha-Calvin of a single crystal or amorphous is made (Y. P.Kudryavtsey, et al., Carbon, 30 (1992) 213).

[0007] Shimoyama and others irradiates laser in a vacuum at the polyvinyl chloride film, and makes clear from a Raman spectrum etc. formation of the Calvin-like carbon material which consists of eight triple bond carbon and 20 double bond carbon (M. Shimoyama, et al., Macromol.Chem., 193 (1992) 569).

[0008] Moreover, composition of the Calvin film in two sorts of approaches is reported (Y. P.Kudryavtsev, et al., Carbon, 30 (1992) 213). (a) It is the film made to condense on the substrate which one uses pure graphite as a target, it carried out the spatter, it is the film which carried out the impact, and which was made from Ar+ ion to coincidence, one besides (b) flew the arc of about 3000 degrees C to two graphite inter-electrode, and carbon was evaporated, and was cooled. (a) It was considered for most film with the single crystal that this was alpha-Calvin. (b) It was shown that the film in which the film was intermingled and the amorphous part and the part which carried out orientation carried out orientation is the method ** type of six.

[0009] The chemical synthetic approach of a carbon material including Calvin is reported in 1973 (V. I.Kasatochikin, et al., Carbon, 11 (1973) 70). According to this report, when dehydrogenation of acetylene is performed in CuCl₂ solution, amorphous carbon including the chain-like polyyne structure (-C^{**}C-C^{**}C-) n and the KYUMUREN structure (=C=C=C=C) n has been obtained. In here, CuCl₂ has also played the role of a dehydrogenation catalyst. It is proved by the analysis of the data of an infrared spectrum that a product is the chain structure. When this product was heated at 1000 degrees C in the vacuum, the homogeneous variant carbon crystal of the new white which saved the chain structure of a carbon macro molecule was obtained. Authors named this "carbyne" which is one of the carbon materials. Electron ray analysis and an X diffraction showed that two variant alpha-Calvin and beta-Calvin existed. alpha phase is a subject, and Calvin obtained from acetylene by the approach of this paper will transfer to beta-Calvin with a more high consistency, if this is processed for 5 minutes at 90kbar(s) and 1800 degrees C.

[0010] Although it expected to carry out polyacetylene chlorination (CHCl) x, to make the halogenation polyacetylene excellent in stereoregularity, to try the dehydrohalogenation, and to obtain KYUMUREN, Calvin of the conjugation triple bond mold of a polyyne mold was obtained. This was concluded from the infrared spectrum. However, it became what did not come to obtain a crystal regular enough and the chain length of n=10-65 mixed as n (-C^{**}C-). (KAkagi, et al., Synth.Metal, 17 (1987) 557).

[0011] Moreover, the approach of compounding a polyyne constituent from acetylene

under oxygen existence using the catalyst which consists of a tertiary amine as cuprous salt and a ligand is indicated (JP,3-44582,B).

[0012] It has reported that the complex which carries out the defluoridation of the polytetrafluoroethylene film in the mercury amalgam of Li, and consists of Calvin and LiF on the surface of the film generates Kavan and others (L. Kavan, Synth.Metal, 58 (1993) 63). LiF is stopping and stabilizing linear Calvin joining together and changing to graphite-like structure (graphite). It seems that however, LiF will move and the Calvin structure will be destroyed if air and water come into complex.

[0013] If chain length is short, the reactivity of an end becomes very high and Calvin's is unstable. Then, the attempt in which annular Calvin will be compounded and isolated has started. Tamaki and others has succeeded in composition of the intermediate field to which six OH radicals were attached to 16 carbocyclic ring by current (the 67th spring annual convention of the Chemical Society of Japan besides Nobuyuki Tamaki, 3L1 (1994) 48).

[0014] The PVDP single crystal film made from the N,N-dimethylformamide solution of poly hooker PINIRIDEN (PVDF) is processed for 40 minutes under a room temperature with 10% potassium ethylate solution of the ethanol which mixed the acetone, is formed into dehydrogen fluoride, and Calvin is obtained (Y. P.Kudryavtsev et al., Carbon, 30 (1992) 213). Although the original PVDF film was a single crystal and it became amorphous, crystallization of Calvin of a KYUMUREN mold arose in 400-degree C annealing among the vacuum, and 30% of the film surface became a single crystal.

[0015] The polytetrafluoroethylene film was returned chemically or electrochemically, the front face was used as the car PON-like ingredient, and the attempt which improves the adhesive property of a film is made for some time (US Patent 3, 967, and 018, 1976:US Patent 3, 296, and 011, and 1967:British Patent 765, 284, and 1957). However, these approaches have the trouble that yield is low, in order to use only a film front face as a KAPON-like ingredient and to obtain a carbon material.

[0016] Although the outline of the synthesis method of the carbon material by which structure was controlled above was described, in order to control structure to altitude, many technical problems are still left behind.

[0017] About physical composition, approaches, such as a resistance heating method, the ion sputtering method, and an arc discharge method, have been used. It is already known by Calvin that there are six or more sorts of anomalies, and much reactant active species are known for 2800K or more elevated temperatures. Or more by 2800K, molecular species, such as C1, C2, C3, C4, and C5, are known, and especially the molecular species of C3 actually generates so much. Therefore, repeatability is good, in order to compound specific Calvin, control of reactant active species is indispensable and development in this field is desired.

[0018] About chemical composition, a approach which builds the conjugation chain by the dehydrohalogenation has been taken from the dehydrogenation polymerization of acetylene, and the hydrocarbon of the shape of a halogenated chain. The former is the dangerous approach of explosion and it is hard to desire future development. As for the latter, it is pointed out that a halogen remains partially. Therefore, development of the approach of progressing a dehydrohalogenation reaction completely is desired.

[0019]

[Problem(s) to be Solved by the Invention] It is difficult the manufacturing method of the

conventional carbon material to obtain the carbon material which controlled structure to altitude in order to require an elevated temperature. Moreover, although fullerene and NANOCHU-PU have been compounded by physical approaches using a high energy beam, such as arc discharge and laser, these approaches are not suitable for industrial extensive composition.

[0020] Therefore, this invention is the temperature near a room temperature or a room temperature, and sets it as the main purposes to offer the technique which can compound industrially the carbon material by which structure was controlled by altitude in large quantities.

[0021]

[Means for Solving the Problem] The result of having repeated research, this invention person caring about the trouble of the conventional technique about composition of the carbon material by which structure was controlled by altitude, The polyolefine derivative or aromatic series condensed-ring hydrocarbon derivative which has the functional group from which it is desorbed as an anion Nitrogen, It faces carrying out electrode electrolytic reduction in inert gas, such as argon gas, and reactant electrodes, such as magnesium, aluminum, and zinc, are set to two electrode methods in the nonaqueous solvent which *****(ed) the supporting electrolyte or the supporting electrolyte, and the energization assistant. As an anode plate Moreover, by using as a counter-electrode in three electrode methods, it succeeded in attaining the above-mentioned purpose.

[0022] :1. following general formula [which is what offers the manufacture approach of the following carbon material] (1) That is, this invention reaches (2).

[0023]

[Formula 3]

[0024] that the inside of a formula, and X1, X2, X3 and X4 are the same, or two or more -- being different from each other -- F -- :X5 which mean Cl, Br, I, H, N+CR one R2R3, SO2R1, and S+R one R2 -- and -- X6 is the same -- or -- being different from each other - - F -- :(however, case where both X5 and X6 are F is removed) R1 which means Cl, Br, I, H, N+CR one R2R3, SO2R1, and S+R one R2, and R2 and R3 it is the same or :n<=50 which means the alkyl group which two or more are different from each other, and is expressed with C_mH_{2m+1} (m<=4). And [0025] [Formula 4]

[0026] (:C 41+2 whose 1 is 1, 2, or 3 among a formula) :X7 which mean the aromatic series condensed-ring hydrocarbon group guided from benzene, naphthalene, an anthracene, a naphthacene, and a pyrene F, Cl, Br, I, H, It is under [nonaqueous organic solvent / which dissolved the supporting electrolyte for at least one sort of a meltable polyolefine oligomer derivative and an aromatic series condensed-ring hydrocarbon derivative] setting. N+CR one R2R3, SO2R1, and S+R one R2 -- meaning -- the organic solvent expressed -- The manufacture approach of the carbon material characterized by being the approach of manufacturing a carbon material by carrying out electrode reduction under an inert gas ambient atmosphere, and using one sort or these alloys of magnesium, zinc, and aluminum as a counter-electrode in three electrode methods as an anode plate in two electrode methods.

[0027] Supporting Electrolyte 2. LiCl, Li₂SO₄, LiBF₄, LiClO₄ and LiPF₆, 4(C₄H₉)NF, (C₄H₉) The manufacture approach of a carbon material given in the above-mentioned term 1 which is at least one sort of 4NCl, 4(C₄H₉)NBr, 4(C₄H₉)NI, 4(C₄H₉)NSO₄, 4(C₄H₉)NBF₄, 4(C₄H₉)NClO₄, and (C₄H₉)NPF₆.

[0028] 3. Manufacture approach of carbon material given in above-mentioned terms 1 or 2 which use supporting electrolyte and energization assistant together.

[0029] 4. Manufacture approach of carbon material given in above-mentioned term 3 whose energization assistant is at least one sort of AlCl₃, FeCl₂, FeCl₃, CoCl₂, CuCl₂, SnCl₂, PdCl₂, VCl₃, and ZnCl₂.

[0030] 5. Manufacture approach of carbon material given in above-mentioned term 1 which uses solvent which contains at least 1 sorts of tetrahydrofuran, N,N-dimethylformamide, N-methyl formamide, formamide, ethylenediamine, 1, and 2-dimethoxyethane and dioxane 10% or more as nonaqueous organic solvent.

[0031]

[Embodiment of the Invention] When an electron moves to the polyolefine derivative or aromatic series condensed-ring hydrocarbon derivative which is a reactant and the functional group which de** is desorbed from the reaction intermediate as an anion, a carbon radical generates the reduction reaction in this invention to a polyolefine derivative or an aromatic series condensed-ring hydrocarbon derivative, and when a next door **** carbon radical carries out coupling, it advances. When this reaction continues, the multiple bond has developed into altitude from the polyolefine derivative or the aromatic series condensed-ring hydrocarbon derivative, and the polymer which leaves the structure of the polyolefine derivative which is a reactant, or an aromatic series condensed-ring hydrocarbon derivative as structure of a macromolecule is obtained.

[0032] The example of a reaction of the tetrafluoroethylene unit in the reactant in the case of using Li for the following scheme as a reducing agent is shown.

[0033]

[Formula 5]

[0034] When a crosslink happens between the obtained oligomer, the macromolecule with which the multiple bond developed into the altitude of a three dimension is obtained. In this invention, a "carbon material" means the oligomer from which the multiple bond developed into altitude, leaving the structure of a polyolefine derivative or an aromatic series condensed-ring hydrocarbon derivative, the oligomer from which the multiple bond developed into those altitude of a three dimension that carried out the crosslink, and a polymer.

[0035] The PORINARE fin derivative and aromatic series condensed-ring hydrocarbon derivative which are used as a reactant by this invention need to have the functional group from which it is desorbed as an anion, and it is expressed with the following

general formula (1) and (2), respectively.

[0036]

[Formula 6]

[0037] that the inside of a formula, and X1, X2, X3 and X4 are the same, or two or more -- being different from each other -- F -- :X5 which mean Cl, Br, I, H, N+CR one R2R3, SO2R1, and S+R one R2 -- and -- X6 is the same -- or -- being different from each other - - F -- :(however, case where both X5 and X6 are F is removed) R1 which means Cl, Br, I, H, N+CR one R2R3, SO2R1, and S+R one R2, and R2 and R3 it is the same or :n<=50 which means the alkyl group which two or more are different from each other, and is expressed with C_mH_{2m+1} (m<=4).

[0038]

[Formula 7]

[0039] (:X7 which mean the aromatic series condensed-ring hydrocarbon group to which :C 41+2 whose l is 1, 2, or 3 is guided from benzene, naphthalene, an anthracene, a naphthacene, and a pyrene mean F, Cl, Br, I, H, N+CR one R2R3, SO2R1, and S+R one R2 among a formula.)

However, since H does not **** in this reaction condition in place ** whose X7 is H in the aromatic series condensed-ring hydrocarbon derivative shown in the polyolefine derivative shown by the general formula (1) by place ** and the general formula (2) whose all of X1, X2, X3, and X4 are H, it removes. although it does not interfere even if it is alike and n and l especially set, as long as it dissolves in a solvent, and it is not limited but it is a big value -- usually -- n -- or less 50 extent -- it is five to about 30 preferably, and l is one to about three. Moreover, although m is not limited especially, either, l to about four are desirable.

[0040] In this invention, it is required to react in inert gas, such as nitrogen and an argon, using a nonaqueous solvent as a solvent.

[0041] As a nonaqueous solvent, a tetrahydrofuran, N,N-dimethylformamide, N-methyl BORUMU amide, a formamide, ethylenediamine, 1, 2-dimethoxyethane, dioxane, etc. are illustrated, it is independent in these one sort, or two or more sorts are used. In a nonaqueous solvent, it is desirable to fully remove water. Moreover, it mixes with other non-drainage system non-proton system solvents, and these nonaqueous solvents can also be used. In such a mixed solvent, it is desirable to contain a nonaqueous solvent 10% or more. As other non-drainage system non-proton system solvents used together with a nonaqueous solvent, dioxane, a trioxane, a furan, 2-methyl furan, tetrahydropyran, a cineole, 1, 2-dimethoxyethane, 1, 2-diethoxy methane, 1, 2-dibutoxy ethane, diethylene-glycol wood ether, diethylene-glycol diethylether, diethylene-glycol dibutyl ether, diethylether, dipropyl ether, diisopropyl ether, dibutyl ether, dihexyl ether, etc. are illustrated.

[0042] In this invention, the combination of a supporting electrolyte and a reactant electrode is important.

[0043] As a supporting electrolyte, LiCl, Li₂SO₄, LiBF₄, LiClO₄ and LiPF₆, 4(C₄H₉)NF, (C₄H₉)₄NCl, 4(C₄H₉)NBr, 4(C₄H₉)NI, 4(C₄H₉)NSO₄, 4(C₄H₉)NBF₄,

4(C₄H₉) NClO₄, and (C₄H₉) 4NPF₆ are used.

[0044] As a reactant electrode (namely, the anode plate in two electrode methods or the counter-electrode in three electrode methods), the alloy of the one sort or these metals of magnesium, zinc, and aluminum is used. Especially as an alloy of these metals, although not limited, a Magnesium alloy ("magnox"; Mg=98.89%, aluminum=1%, calcium=0.1%, Ba=0.01%), an aluminium alloy ("duralumin"; aluminum=95%, Cu=4.6%, Mg=0.5%), a zinc-aluminium alloy (Zn=78%, aluminum=22%), etc. are illustrated.

[0045] Moreover, when the conductivity of the solution which dissolved the supporting electrolyte is high, it is not indispensable, but when conductivity is low, it is desirable to use an energization assistant. As an energization assistant, one sort, such as AlCl₃, FeCl₂, FeCl₃, CoCl₂, CuCl₂, SnCl₂, PdCl₂, VCl₃, and ZnCl₂, or two sorts or more are used. The concentration of an energization assistant is not limited as long as predetermined conductivity is obtained.

[0046] Although especially electrolytic reduction conditions are not limited, for example, they make about [3-30V] potential impress and react to inter-electrode over about 5 - 10 hours at about 0 degree C among desiccation inert gas ambient atmospheres, such as N₂, Ar, and helium. Although potential is high, resistance of reaction mixture is high, and since the potential fall inside reaction mixture is large, the potential of this level is required of this invention.

[0047] The mechanism of the reduction reaction in this invention is complicated.

Reduction of the polyolefine derivative according [reduction] to the direct contact to (1) electrode or an aromatic series condensed-ring hydrocarbon derivative, (2) In reduction of the polyolefine derivative by the cation of the supporting electrolyte returned by the electrode or an aromatic series condensed-ring hydrocarbon derivative, and (3) 2 electrode method as an anode plate The magnesium used as a counter-electrode in three electrode methods, zinc, aluminum, or its alloy It dissolves as a cation and this is returned with an electrode, and it is carried out when three reactions called reduction of the polyolefine derivative by this reductant or an aromatic series condensed-ring hydrocarbon derivative advance to coincidence.

[0048] In a reduction reaction (2) and (3), since a reduction reaction advances in a solution, rather than the case where the reaction of (1) in the usual electrode reduction is used, it is efficient and a carbon material can be manufactured by high yield and short reaction time. Moreover, the cation of the energization assistant used if needed is also returned with an electrode, and this reductant returns a polyolefine derivative or an aromatic series condensed-ring hydrocarbon derivative.

[0049] Or it is, at chemical reduction, a carbon material can be manufactured by this invention approach as compared with reacting to the bottom of heating using the reducing agent which is danger and which handling takes cautions by the electrode reduction reaction [carry / at a room temperature / it / and] with little risk.

[0050] The ingredient of the cathode in two electrode methods and the working electrode in three electrode methods, especially a configuration, etc. are not limited. Platinum, gold, stainless steel, etc. can be used as these ingredients. Moreover, an electrode configuration can choose the configuration of arbitration, such as a wire, a mesh, and a plate.

[0051] Moreover, during electrolytic reduction, the polarity of impression potential can be changed once or more between a working electrode and a counter-electrode in three

electrode methods between cathode and an anode plate in two electrode methods. It is also possible to control by this, generating evils, such as a fall of the reaction rate which is easy to produce with advance of a reaction, and increase of side reaction, since the impurity on an electrode surface etc. can be removed. What is necessary is just to perform the count of a change the suitable number of times at proper spacing if needed, so that these evils may be controlled.

[0052] The carbon material obtained by this invention fits application in various fields using the outstanding property. For example, the aerospace and the charge of nuclear-fusion device material using the rate of sliding ingredient; quantity heatproof high elasticity using high abrasion resistance; it is useful as an optical-fiber ingredient for skyscraper members etc. In addition, the carbon material obtained by this invention is useful as a raw material of carbon materials, such as a diamond, a carbon nanotube, and fullerene.

[0053]

[Effect of the Invention] According to this invention approach, it becomes possible to manufacture industrially the carbon material by which structure was controlled by altitude in the bottom atmospheric pressure of a room temperature in large quantities. Moreover, since the structure of the carbon material which is a compost is decided by structure of the polyolefine derivative which is a reactant, or an aromatic series condensed-ring hydrocarbon, it can control the structure of a carbon material to altitude by choosing a reactant.

[0054]

[Example] An example is shown below and the place by which it is characterized [of this invention] is clarified further.

[0055] The tetrahydrofuran which dissolved CH₂=CH(CF₂)₈ CH=CH₂ (referred to as "DVHDFO" below 1 and 8-divinyl HEKISADEKA fluoro octane;), LiCl, and FeCl₃ of the presentation shown in Table 1 in 3 ROFURASUKO of 130ml of examples was taught. The commercial dehydration tetrahydrofuran was further dried and used for the tetrahydrofuran by the molecular sieve, and the anhydride was all used for LiCl and FeCl₃.

[0056] It connected with the low-battery power source, having put in in the flask the stainless steel (SUS304) plate furnished with the lead wire of cathode, and magnesium RIPON which attached the lead wire of an anode plate on the occasion of the reaction, and maintaining confidentiality through the rubber stopper of a flask. It electrolyzed by 4V, agitating with a stirrer chip, after exchanging the interior of a flask for nitrogen gas. 8 hours after, black precipitate was obtained. When this was analyzed by FT-IR, the absorption band (1630cm⁻¹) of C=C and the absorption band (2100cm⁻¹) of C**C which were not seen were observed by DVHDPO. Moreover, absorption of the absorption band (1400cm⁻¹) of C-F seen by DVHDFO was decreasing remarkably. These results show that the carbon material was compounded by this invention approach.

[0057] The carbon material was compounded like the example 1 except using the aluminum ribbon furnished with example 2 lead wire as an anode plate. In IR analysis of the obtained ingredient, the absorption band of C=C and the absorption band of C**C were observed, and absorption of the absorption band of C-F was decreasing remarkably. These results show that the carbon material was compounded.

[0058] The carbon material was compounded like the example 1 except using the zinc

ribbon furnished with example 3 lead wire as an anode plate. In IR analysis of the obtained ingredient, the absorption band of C=C and the absorption band of C**C were observed, and absorption of the absorption band of C-F was decreasing remarkably. These results show that the carbon material was compounded.

[0059]

[Table 1]

[0060] Notes: The notation in Table 1 and each following table thru/or the declared semantics are as follows.

[0061] 1) In the case of two electrodes, mean an anode plate, and, in the case of three electrodes, mean a counter-electrode.

[0062] 2) In the case of two electrodes, mean cathode, and, in the case of three electrodes, mean a working electrode.

[0063] 3) 1, 8-divinyl HEKISADEKA fluoro octane 4strong; a strong absorption band is observed.

[0064] medium; the absorption band of whenever [middle] is observed.

[0065] weak; a weak absorption band is observed.

[0066] none; an absorption band is not observed.

[0067] Although the carbon material was compounded like the example 1 except using the stainless steel (SUS304) ribbon furnished with example of comparison 1 lead wire as an anode plate, black precipitate which was obtained in the example 1 was not obtained. Moreover, in IR analysis of a product, the absorption band of C=C was not observed and reduction of the absorption band of C-F was not accepted, either.

[0068] It is clear that a reaction does not advance, when not using the magnesium which dissolves in electrolysis reaction time and participates in a reduction reaction from contrast of the result of examples 1-3, and the result of the example 1 of a comparison, aluminum, and an ingredient like zinc as an anode plate.

[0069] The carbon material was compounded like the example 1 except using the Magnesium alloy ("magno KUSSU":Mg=98.89%, aluminum=1%, calcium=0.1%,

Be=0.01%) plate furnished with example 4 lead wire as an anode plate. In IR analysis of the obtained ingredient, the absorption band of C=C and the absorption band of C**C were observed, and absorption of the absorption band of C-F was decreasing remarkably. These results show that the carbon material was compounded.

[0070] The carbon material was compounded like the example 1 except using the aluminium alloy ("duralumin":aluminum=95%, Cu=4%, Mg=0.5%, Mn=0.5%) plate furnished with example 5 lead wire as an anode plate. In IR analysis of the obtained ingredient, the absorption band of C=C and the absorption band of C**C were observed, and absorption of the absorption band of C-F was decreasing remarkably. These results show that the carbon material was compounded.

[0071]

[Table 2]

[0072] The carbon material was compounded like the example 1 except using the zinc-aluminium alloy (Zn=78%, aluminum=22%) plate furnished with example 6 lead wire as an anode plate. In IR analysis of the obtained ingredient, the absorption band of C=C and the absorption band of C**C were observed, and absorption of the absorption band of C-F was decreasing remarkably. These results show that the carbon material was compounded.

[0073] The carbon material was compounded like the example 1 except using the platinum plate furnished with example 7 lead wire as cathode. In IR analysis, the absorption band of C=C and the absorption band of C**C were observed, and absorption of the absorption band of C-F was decreasing remarkably. These results show that the carbon material was compounded.

[0074] The carbon material was compounded like the example 1 except using as cathode the metal plate which attached example 8 lead wire. In IR analysis, the absorption band of C=C and the absorption band of C**C were observed, and absorption of the absorption band of C-F was decreasing remarkably. These results show that the carbon material was compounded.

[0075]
[Table 3]

[0076] As long as the result shown in examples 1, 7, and 8 is a conductive ingredient about the cathode in this invention, it is shown that there is no limit.

[0077] an example 9 -- the carbon material was compounded like the example 1 except using as a solvent the N,N-dimethylformamide beforehand dried using the molecular sieve. In IR analysis, the absorption band of C=C and the absorption band of C**C were observed, and absorption of the absorption band of C-F was decreasing remarkably. These results show that the carbon material was compounded.

[0078] an example 10 -- the carbon material was compounded like the example 1 except using as a solvent N-methyl formamide beforehand dried using the molecular sieve. In IR analysis, the absorption band of C=C and the absorption band of C**C were observed, and absorption of the absorption band of C-F was decreasing remarkably. These results show that the carbon material was compounded.

[0079] an example 11 -- the carbon material was compounded like the example 1 except using as a solvent the formamide beforehand dried using the molecular sieve. In IR analysis, the absorption band of C=C and the absorption band of C**C were observed, and absorption of the absorption band of C-F was decreasing remarkably. These results show that the carbon material was compounded.

[0080]
[Table 4]

[0081] an example 12 -- the carbon material was compounded like the example 1 except using as a solvent the ethylenediamine beforehand dried using the molecular sieve. In IR analysis, the absorption band of C=C and the absorption band of C**C were observed, and absorption of the absorption band of C-F was decreasing remarkably. These results show that the carbon material was compounded.

[0082] an example 13 -- the carbon material was compounded like the example 1 except using as a solvent 1 and 2-dimethoxyethane beforehand dried using the molecular sieve. In IR analysis, the absorption band of C=C and the absorption band of C**C were observed, and absorption of the absorption band of C-F was decreasing remarkably. These results show that the carbon material was compounded.

[0083] an example 14 -- the carbon material was compounded like the example 1 except using as a solvent the dioxane beforehand dried using the molecular sieve. In IR analysis, the absorption band of C=C and the absorption band of C**C were observed, and absorption of the absorption band of C-F was decreasing remarkably. These results show that the carbon material was compounded.

[0084]

[Table 5]

[0085] The carbon material was compounded like the example 1 except using as a solvent the mixture which consists of a tetrahydrofuran (50vol.%) dried using example 15 molecular sieve, respectively, and ethylene glycol diethylether (50vol.%). In IR analysis, the absorption band of C=C and the absorption band of C**C were observed, and absorption of the absorption band of C-F was decreasing remarkably. These results show that the carbon material was compounded.

[0086] The carbon material was compounded like the example 1 except using as a solvent the mixture which consists of a tetrahydrofuran (10vol.%) dried using example 16 molecular sieve, respectively, and ethylene glycol diethylether (90vol.%). In IR analysis, the absorption band of C=C and the absorption band of C**C were observed, and absorption of the absorption band of C-F was decreasing remarkably. These results show that the carbon material was compounded.

[0087] The carbon material was compounded like the example 1 except using example of comparison 2 ethyl alcohol as a solvent. The solvent added CaH2 beforehand, and reflux and after distilling, it dried it using the molecular sieve. However, black precipitate which was obtained in the example 1 was not obtained. Moreover, in IR analysis of a product, the absorption band of C=C was not observed and reduction of the absorption band of C-F was not accepted, either.

[0088] In using an ethyl alcohol solvent, it turns out that composition of the carbon material by reduction of DVHDFO cannot be performed.

[0089] The carbon material was compounded like the example 1 except using the example triacetic acid ethyl of a comparison as a solvent. The solvent added CaH2 beforehand, and reflux and after distilling, it dried it using the molecular sieve. However, black precipitate which was obtained in the example 1 was not obtained. Moreover, in IR analysis of a product, the absorption band of C=C was not observed and reduction of the absorption band of C-F was not accepted, either.

[0090] In using ethyl acetate, it turns out that composition of the carbon material by reduction of DVHDFO cannot be performed.

[0091] the example 4 of a comparison -- the carbon material was compounded like the example 1 except using as a solvent the chloroform beforehand dried using the molecular sieve. However, black precipitate which was obtained in the example 1 was not obtained. Moreover, in IR analysis of a product, the absorption band of C=C was not observed and reduction of the absorption band of C-F was not accepted, either.

[0092] In using chloroform, it turns out that composition of the carbon material by reduction of DVHDFO cannot be performed.

[0093]

[Table 6]

[0094] When using non-drainage system non-proton system organic solvents, such as a tetrahydrofuran, N,N-dimethylformamide, N-methyl formamide, a formamide, ethylenediamine, 1, 2-dimethoxyethane, and dioxane, putting the result of an example 1, examples 9-16, and the examples 2-4 of a comparison together, it is clear from DVHDFO that a carbon material is compounded. In the system of reaction of this invention, it is guessed that this is a thing related to whether for the reducing agent generated in the electrode surface, for example, aluminum, Mg, Zn, Li, etc., to carry out a solvation, and to be stabilized.

[0095] Except using LiSO₄ as example 17 supporting electrolyte, when the carbon material was compounded like the example 1, black precipitate was obtained 8 hours after. In IR analysis, the absorption band of C=C and the absorption band of C**C were observed, and absorption of the absorption band of C-F was decreasing remarkably.

These results show that the carbon material was compounded.

[0096] Except using LiBF₄ as example 18 supporting electrolyte, when the carbon

material was compounded like the example 1, black precipitate was obtained 8 hours after. In IR analysis, the absorption band of C=C and the absorption band of C**C were observed, and absorption of the absorption band of C-F was decreasing remarkably. These results show that the carbon material was compounded.

[0097] Except using LiCl4 as example 19 supporting electrolyte, when the carbon material was compounded like the example 1, black precipitate was obtained 8 hours after. In IR analysis, the absorption band of C=C and the absorption band of C**C were observed, and absorption of the absorption band of C-F was decreasing remarkably. These results show that the carbon material was compounded.

[0098]

[Table 7]

[0099] Except using LiPF6 as example 20 supporting electrolyte, when the carbon material was compounded like the example 1, black precipitate was obtained 8 hours after. In IR analysis, the absorption band of C=C and the absorption band of C**C were observed, and absorption of the absorption band of C-F was decreasing remarkably. These results show that the carbon material was compounded.

[0100] Except using 4NF as example 21 supporting electrolyte (C4H9), when the carbon material was compounded like the example 1, black precipitate was obtained 8 hours after. In IR analysis, the absorption band of C=C and the absorption band of C**C were observed, and absorption of the absorption band of C-F was decreasing remarkably.

These results show that the carbon material was compounded.

[0101] Except using 4NCl as example 22 supporting electrolyte (C4H9), when the carbon material was compounded like the example 1, black precipitate was obtained 8 hours after. In IR analysis, the absorption band of C=C and the absorption band of C**C were observed, and absorption of the absorption band of C-F was decreasing remarkably.

These results show that the carbon material was compounded.

[0102]

[Table 8]

[0103] Except using 4NBr as example 23 supporting electrolyte (C4H9), when the carbon material was compounded like the example 1, black precipitate was obtained 8 hours after. In IR analysis, the absorption band of C=C and the absorption band of C**C were observed, and absorption of the absorption band of C-F was decreasing remarkably.

These results show that the carbon material was compounded.

[0104] Except using 4NI as example 24 supporting electrolyte (C4H9), when the carbon material was compounded like the example 1, black precipitate was obtained 8 hours after. In IR analysis, the absorption band of C=C and the absorption band of C**C were observed, and absorption of the absorption band of C-F was decreasing remarkably.

These results show that the carbon material was compounded.

[0105] Except using 4NSO4 as example 25 supporting electrolyte (C4H9), when the carbon material was compounded like the example 1, black precipitate was obtained 8 hours after. In IR analysis, the absorption band of C=C and the absorption band of C**C were observed, and absorption of the absorption band of C-F was decreasing remarkably.

These results show that the carbon material was compounded.

[0106]

[Table 9]

[0107] Except using 4NBF₄ as example 26 supporting electrolyte (C₄H₉), when the carbon material was compounded like the example 1, black precipitate was obtained 8 hours after. In IR analysis, the absorption band of C=C and the absorption band of C**C were observed, and absorption of the absorption band of C-F was decreasing remarkably. These results show that the carbon material was compounded.

[0108] Except using 4NCIO₄ as example 27 supporting electrolyte (C₄H₉), when the carbon material was compounded like the example 1, black precipitate was obtained 8 hours after. In IR analysis, the absorption band of C=C and the absorption band of C**C were observed, and absorption of the absorption band of C-F was decreasing remarkably. These results show that the carbon material was compounded.

[0109] Except using 4NPF₆ as example 28 supporting electrolyte (C₄H₉), when the carbon material was compounded like the example 1, black precipitate was obtained 8 hours after. In IR analysis, the absorption band of C=C and the absorption band of C**C were observed, and absorption of the absorption band of C-F was decreasing remarkably. These results show that the carbon material was compounded.

[0110]

[Table 10]

[0111] Except using the same weight mixture of LiCl and 4(C₄H₉)NCl as example 29 supporting electrolyte, when the carbon material was compounded like the example 1, black precipitate was obtained 8 hours after. In IR analysis, the absorption band of C=C and the absorption band of C**C were observed, and absorption of the absorption band of C-F was decreasing remarkably. These results show that the carbon material was compounded.

[0112] Except using the same weight mixture of LiBF₄ and 4(C₄H₉)NBF₄ as example 30 supporting electrolyte, when the carbon material was compounded like the example 1, black precipitate was obtained 8 hours after. In IR analysis, the absorption band of C=C and the absorption band of C**C were observed, and absorption of the absorption band of C-F was decreasing remarkably. These results show that the carbon material was compounded.

[0113] Composition of a carbon material was tried like the example 1 except not using example of comparison 5 supporting electrolyte. However, black precipitate was not obtained 8 hours after. Moreover, in IR analysis of reaction mixture, the strong absorption band of C-F was observed to no absorption bands of C=C and absorption bands of C**C having been observed.

[0114] The synthetic conditions for which this result does not use a supporting electrolyte show that a carbon material is not compounded. When not using a supporting electrolyte, resistance of a reaction solution is strong, the potential difference does not arise in an electrode surface, but it is guessed that this is what is depended on the reducibility active substance by electrode reaction not being generated.

[0115]

[Table 11]

[0116] It is indispensable to use at least one sort of a supporting electrolyte in the synthesis method of the carbon material by this invention so that clearly from the result obtained in an example 1, examples 17-30, and the example 5 of a comparison. [0117] Except using AlCl₃ as an example 31 energization assistant, when the carbon material was compounded like the example 1, black precipitate was obtained 8 hours after. In IR analysis, the absorption band of C=C and the absorption band of C**C were observed, and absorption of the absorption band of C-F was decreasing remarkably. These results show that the carbon material was compounded.

[0118] Except using FeCl₂ as an example 32 energization assistant, when the carbon material was compounded like the example 1, black precipitate was obtained 8 hours after. In IR analysis, the absorption band of C=C and the absorption band of C**C were observed, and absorption of the absorption band of C-F was decreasing remarkably. These results show that the carbon material was compounded.

[0119] Except using CoCl₂ as an example 33 energization assistant, when the carbon material was compounded like the example 1, black precipitate was obtained 8 hours after. In IR analysis, the absorption band of C=C and the absorption band of C**C were observed, and absorption of the absorption band of C-F was decreasing remarkably. These results show that the carbon material was compounded.

[0120]

[Table 12]

[0121] Except using CuCl₂ as an example 34 energization assistant, when the carbon material was compounded like the example 1, black precipitate was obtained 8 hours after. In IR analysis, the absorption band of C=C and the absorption band of C**C were observed, and absorption of the absorption band of C-F was decreasing remarkably. These results show that the carbon material was compounded.

[0122] Except using SnCl₂ as an example 35 energization assistant, when the carbon material was compounded like the example 1, black precipitate was obtained 8 hours after. In IR analysis, the absorption band of C=C and the absorption band of C**C were observed, and absorption of the absorption band of C-F was decreasing remarkably. These results show that the carbon material was compounded.

[0123] Except using PdCl₂ as an example 36 energization assistant, when the carbon material was compounded like the example 1, black precipitate was obtained 8 hours after. In IR analysis, the absorption band of C=C and the absorption band of C**C were observed, and absorption of the absorption band of C-F was decreasing remarkably. These results show that the carbon material was compounded.

[0124]

[Table 13]

[0125] Except using VCl₃ as an example 37 energization assistant, when the carbon material was compounded like the example 1, black precipitate was obtained 8 hours after. In IR analysis, the absorption band of C=C and the absorption band of C**C were observed, and absorption of the absorption band of C-F was decreasing remarkably. These results show that the carbon material was compounded.

[0126] Except using ZnCl₂ as an example 38 energization assistant, when the carbon material was compounded like the example 1, black precipitate was obtained 8 hours after. In IR analysis, the absorption band of C=C and the absorption band of C**C were observed, and absorption of the absorption band of C-F was decreasing remarkably. These results show that the carbon material was compounded.

[0127] Except using the same weight mixture of AlCl₃ and FeCl₃ as an example 39 energization assistant, when the carbon material was compounded like the example 1, black precipitate was obtained 8 hours after. In IR analysis, the absorption band of C=C and the absorption band of C**C were observed, and absorption of the absorption band of C-F was decreasing remarkably. These results show that the carbon material was compounded.

[0128]

[Table 14]

[0129] Except using the same weight mixture of CuCl₂ and FeCl₃ as an example 40 energization assistant, when the carbon material was compounded like the example 1, black precipitate was obtained 8 hours after. In IR analysis, the absorption band of C=C and the absorption band of C**C were observed, and absorption of the absorption band of C-F was decreasing remarkably. These results show that the carbon material was compounded.

[0130] Except not using an example 41 energization assistant, when the carbon material was compounded like the example 1, black precipitate was obtained 8 hours after. In IR analysis, the absorption band of C=C and the absorption band of C**C were observed, and absorption of the absorption band of C-F was decreasing remarkably. These results show that the carbon material was compounded. However, absorption is not large, although the absorption band of C-F is observed clearly and the absorption band of C**C is observed. Therefore, in an electrolysis resultant, that in which a part of unreacted part remains with the carbonization part is conjectured.

[0131] As example 42 supporting electrolyte (C₄H₉), when the carbon material was compounded like the example 1 except not using an energization assistant, using 9NBF₄, black precipitate was obtained 8 hours after. In IR analysis, the absorption band of C=C and the absorption band of C**C were observed, and absorption of the absorption band of C-F was decreasing remarkably. These results show that the carbon material was compounded. However, absorption is not large, although the absorption band of C-F is observed clearly and the absorption band of C**C is observed. Therefore, in an electrolysis resultant, that in which a part of unreacted part remains with the carbonization part is conjectured.

[0132] Composition of a carbon material was tried like the example 1 except not using example of comparison 6 supporting electrolyte, and an energization assistant. However, black precipitate was not obtained 8 hours after. Moreover, in IR analysis of reaction mixture, the strong absorption band of C-F was observed to no absorption bands of C=C and absorption bands of C**C having been observed.

[0133] This result shows that a carbon material is not compounded under the conditions of this example of a comparison. Since this has strong resistance of a reaction solution, it is guessed that it is what is depended on electrode reaction having not progressed.

[0134]

[Table 15]

[0135] Also when conductivity sufficient with just a supporting electrolyte is not obtained from the result obtained in an example 1, examples 31-42, and the example 6 of a comparison, it is clear by adding an energization assistant to a solvent that a carbon material is obtained. That is, each having carbon-ized DVHDO used as a reactant black in an example 1 and examples 31-42, and having carbon-ized also in IR analysis was checked.

[0136] By compounding a carbon material like an example 1, black precipitate was obtained after the 8:00 question except using perfluoro hexyl iodide (PFHI) as example 43 reactant. In IR analysis, although the absorption band of C=C was observed, the absorption band of C**C was not observed. It is clear from such observation that the polyacetylene's carbon material was compounded.

[0137] By compounding a carbon material like an example 1, black precipitate was obtained after the 8:00 question except using perfluoro octyl iodide (PFOI) as example 44 reactant. In IR analysis, the absorption band of C=C and the absorption band of C**C were observed. Thereby, it was checked that the carbon material had been compounded.

[0138] By compounding a carbon material like an example 1, black precipitate was obtained after the 8:00 question except using perfluoro DESHIRU iodide (PFDI) as example 45 reactant. In IR analysis, the absorption band of C=C and the absorption band of C**C were observed. Thereby, it was checked that the carbon material had been compounded.

[0139]

[Table 16]

[0140] By compounding a carbon material like an example 1, black precipitate was obtained after the 8:00 question except using perfluoro decylethylene (PFDE) as example 46 reactant. In IR analysis, although the absorption band of C=C was observed, the absorption band of C**C was not observed. Thereby, it was checked that the polyacetylene's carbon material had been compounded.

[0141] By compounding a carbon material like an example 1, black precipitate was obtained after the 8:00 question except using hexafluoro benzene (HFB) as example 47 reactant. In IR analysis, the absorption band of C=C and the absorption band of C**C were observed. Thereby, it was checked that the carbon material had been compounded.

[0142] By compounding a carbon material like an example 1, black precipitate was obtained after the 8:00 question except using hexabromobenzene (HBB) as example 48 reactant. In IR analysis, the absorption band of C=C and the absorption band of C**C were observed. Thereby, it was checked that the carbon material had been compounded.

[0143]

[Table 17]

[0144] By compounding a carbon material like an example 1, black precipitate was obtained after the 8:00 question except using octafluoro naphthalene (OFN) as example 49 reactant. In IR analysis, the absorption band of C=C and the absorption band of C**C were observed. Thereby, it was checked that the carbon material had been compounded.

[0145] Black precipitate was obtained after the 8:00 question by compounding a carbon material like an example 1 except using the dodeca fluoro -1 and 6-diido hexane (DFDIH) as example 50 reactant. In IR analysis, the absorption band of C=C and the absorption band of C**C were observed. Thereby, it was checked that the carbon material had been compounded.

[0146] Black precipitate was obtained after the 8:00 question by compounding a carbon material like an example 1 except using the hexa deca fluoro -1 and 8-diiodo octane (HFDOI) as an example 51 reactant. In IR analysis, the absorption band of C=C and the absorption band of C**C were observed. Thereby, it was checked that the carbon material had been compounded.

[0147] Although composition of a carbon material was tried like the example 1 except using an OKUTA decane (OD) as example of comparison 7 reactant, black precipitate was not obtained 8 hours after. In IR analysis, absorption PANDO of C=C and the absorption band of C**C were not observed, but it was checked that the carbon material had not been compounded.

[0148] Although composition of a carbon material was tried like the example 1 except using benzene (BN) as example of comparison 8 reactant, black precipitate was not obtained 8 hours after. In IR analysis, absorption PANDO of C=C and the absorption band of C**C were not observed, but it was checked that the carbon material had not been compounded.

[0149]

[Table 18]

[0150] In this invention, it is indispensable to have the functional group from which a reactant may be desorbed as an anion so that clearly from contrast with examples 43-51 and the examples 7-8 of a comparison.

[0151] The carbon material was compounded with three electrode methods like the example 1 by using magnesium as a counter-electrode, using a gold streak respectively as a reference electrode, having used example 52 stainless steel as the operation pole. 2.2V were impressed between the operation pole and the reference electrode. Black precipitate was obtained 8 hours after reaction initiation. In IR analysis, the absorption band of C=C and the absorption band of C**C were observed. Thereby, it was checked that the carbon material had been compounded.

[0152] According to three electrode methods, since it was more compoundable by low voltage, it was safe, and was larger than the case where absorption of C**C is two electrode methods, and the compost to which the reduction reaction advanced more was obtained.

[0153] The carbon material was compounded like the example 1, changing the polarity of an anode plate and cathode according to the schedule of the following table 19 during an example 53 composition reaction.

[0154]

[Table 19]

[0155] Black precipitate was obtained 5 hours after reaction initiation, and the compost was obtained for a short time as compared with the case where a polar change is not performed. In IR analysis, the absorption band of C=C and the absorption band of C**C were observed, and it was checked that the carbon material had been compounded.

[0156]

[Table 20]